January 2000

FINAL REPORT 1995-1999
Smart Materials by Extrusion Solid Freeform Fabrication
AASERT F49620-95-1-0393 DEF

Paul Calvert
Department of Materials Science and Engineering
University of Arizona, Tucson AZ 85721

EXECUTIVE SUMMARY
During the period of this project, rapid prototyping emerged as a versatile new process for manufacturing small numbers of components. Based on our previous work on biomimetic materials, we realized that the layerwise building process of rapid prototyping has much in common with biological growth. This suggested that the method could not only be used to make parts from existing materials but could be used to make wholly new materials and materials combinations. We identified as goals a number of materials that exist in biology but have no synthetic equivalents. These include strong bone-like composite materials, cuticle-like materials with large number of embedded mechanical and chemical sensors, materials with internal property gradients and muscle-like materials. Progress on the first three is described in the published papers listed below, the last of these was studied under ARO funding and is also published.

We have had a close collaboration with Advanced Ceramics Research of Tucson AZ in this area, and have worked with them on projects for NASA, DARPA, ONR and the ARO. These efforts have led to two issued patents, listed below. In addition, Hugh Denham is now finishing his thesis at Sandia National Labs., where another joint patent is pending. A joint project with Lockheed Martin at Palmdale concerns embedded sensors in composite panels.

The following narrative outlines some of these efforts and provides a brief opinion of the outlook for rapid prototyping of new materials. Publications, interactions with other organizations and personnel are listed at the end.

SMART MATERIALS BY EXTRUSION SOLID FREEFORM FABRICATION

TECHNICAL PROGRESS

Freeform fabrication methods were used to build organic-inorganic hybrid materials by the repetitive addition of thin layers. In principle, these methods are very applicable to sol-gel glasses and organic-inorganic hybrids where diffusion and shrinkage during solidification are important. The chemical conversion of metal alkoxides to oxides may require the diffusion of water into the part and does require the diffusion out of the alcohol reaction products. If this conversion can occur in the layers as they form, the diffusion paths are short and so the reaction rate should be much higher. The conversion of alkoxide to oxide also involves a large reduction in volume, which can be accommodated in elastomers but leads to distortion and cracking of thick, rigid parts. Again, conversion layer by layer may eliminate these effects. We used extrusion freeform fabrication to make bars of mineralized gel, of silicate glass and of methacrylate-silica hybrids. Good mechanical properties could be attained in each case, with up to 50 vol.% inorganic phase and bend strengths in the range from 50-100 MPa. We became convinced that a swelling and deswelling process is essential to obtaining high volume fractions of mineral in a polymer matrix.

Layerwise processing methods were used to build parts with sensors placed within the structure and fully embedded. Previously, blocks of epoxy resin had been formed with embedded optical fibers. This fiber can be used to monitor curing and water uptake of the epoxy using ambient light which passes through the resin, is collected by the fiber and analyzed in a near-IR spectrometer. More recently, piezoelectric polymer films were embedded in epoxy and used to monitor curing by changes in response to an external stress pulse. In the long run it would be desirable to form parts containing many sensors with sensitivity differing environmental variables. Epoxy parts have also been freeformed with lines of conducting carbon-filled polymer written into the structure during forming. Where they are at the surface of the part, these materials respond to solvent exposure by a resistance change. Parts have been made with sensors distributed across the surface and their ability to sense gradients of solvent vapor, and so direction to a source, was demonstrated.

A series of metal matrix composites have been formed by extrusion freeform fabrication of a sinterable aluminum alloy in combination with silicon carbide particles and whiskers, carbon fibers, alumina particles and hollow flyash cenospheres. Silicon carbide particles were most successful in that the composites retained high density with up to 20 vol.% of reinforcement. The strength increased 60% above the strength of the metal matrix alone and the elastic modulus doubled. Comparison with simple models suggests that this unexpectedly high degree of reinforcement can be attributed to the concentration of small silicon carbide particles around the larger metal powder. This method allows composites to be formed with hollow spheres that cannot be formed by other powder or melt methods.

Extrusion freeform fabrication was used to make bars of glass fiber reinforced epoxy resin. The short fibers, aspect ratio 7, are largely aligned parallel to the direction of motion of the write head which deposits the resin. The degree of alignment increases as the write head speed increases

and the resin stream is extended further. The elastic modulus also increases with alignment. If the writing direction is inclined to the bar axis, the modulus decreases to an extent comparable with that predicted for a fully aligned composite. Carbon fiber and clay composites have been formed similarly and moduli up to 18 GPa have been achieved.

Layerwise manufacturing methods for conventional plastic parts are limited by properties, precision and speed. Both stereolithography and fused deposition modeling result in weak parts, the former due to the brittle cross-linked resins and the latter due to poor interlayer bonding. Properties could be much improved if a reinforced epoxy feedstock was developed. Precision can be enhanced by reducing the layer thickness but the manufacturing time climbs in proportion to the number of layers. However, a simple post-machining on the same apparatus could allow thicker layers with good precision. The obvious material goal would then be a composite with properties comparable to machined aluminum. This would allow freeforming to become desktop manufacturing. Also, a lighter composite could replace many small aluminum parts in aircraft and automobiles.

In terms of new materials, freeforming methods could be used to make tough ceramics, sensing and actuating materials and parts where several different materials need to be integrated. Here the potential is great but most possible applications are based on new design approaches and so will not be implemented in the short term. One area where freeforming can be expected to expand its use is in medical implants. Here precision is not a major issue, many parts need to be tailored to the individual patient and complex structures, especially porous structures, may perform much better than simple monoliths.

MANUSCRIPTS PUBLISHED

J. Lombardi, G. George, L. Rintoul and P. Calvert, "Freeform fabrication of polymers and composites" Polymer Preprints 37(1) 221-222 (1996)

P. Calvert, G. George and L. Rintoul, "Monitoring of cure and water uptake in a freeformed epoxy resin by an embedded optical fiber"*Chem. Mater.*, *8* (1996) 1298-1301.

H. Grijalva, M. Inoue, S. Boggavarapu, P. Calvert, "Films of amorphous and crystalline copper sulfides, CuS" J. Mater. Chem. 6 (1996) 1157-1160.

P.Calvert "Potential applications of nanotubes" in Carbon Nanotubes, preparation and properties ed. T.W. Ebbesen, CRC Press, Boca Raton FL, 1997 pp. 277-292

R.S.Crockett & P. D. Calvert "The liquid-to-solid transition in stereodeposition techniques" in Solid Freeform Fabrication Proceedings 1996 eds. H.L. Marcus, J.J. Beaman, D.L. Bourell, J.W. Barlow and R.H. Crawford, U. Texas, Austin pp. 257-264

H. Denham, G. George, L. Rintoul, P. Calvert, "Fabrication of polymers and composites containing embedded sensors." Proceedings of the SPIE - The International Society for Optical

Engineering 2779 (1996) p742-7.

P. Calvert, R. Crockett, "Chemical solid free-form fabrication: making shapes without molds" Chem. Mater. 9 650-663 (1997)

J. O'Kelly, R. Crockett, H. Martin & Paul Calvert, "Biomimetic processing of gel glasses and organic-inorganic hybrids" J. Sol-gel Sci. & technology (1997) 8 641-644

H.B.Denham, T.A. Anderson, E. Madenci & Paul Calvert, "Embedded PVF2 sensors for smart composites" SPIE Proceedings 3040 (1997) 138-147

J. Cesarano, T. A. Baer and P. Calvert "Recent developments in freeform fabrication of dense ceramics from slurry deposition" in Solid Freeform Fabrication Proceedings 1997 eds. D.L. Bourell, J.J. Beaman, R.H. Crawford, H.L. Marcus and J.W. Barlow, U. Texas, Austin pp. 25-32

R.S. Crockett, P.D. Calvert "Rheology and Freeform Fabrication: Modeling Material Flow in Deposition Techniques" in Solid Freeform Fabrication Proceedings 1997 eds. D.L. Bourell, J.J. Beaman, R.H. Crawford, H.L. Marcus and J.W. Barlow, U. Texas, Austin pp. 717-724

P. Calvert, J. Frechette, C. Souvignier, "Mineralization of multilayer hydrogels as a model for mineralization of bone" Mater. Res. Soc. Symp. Proc. 489 "Materials Science of the Cell" eds. B. Mulder, C.F. Schmidt, V. Vogel, 1998, pp.153-160

P. Calvert, "Freeforming of polymers" Curr. Opinion in Sol. St. & Mater. Sci. 3, 585-588 (1998)

P.Calvert, J. O'Kelly, C. Souvignier, "Solid Freeform Fabrication Of Organic-Inorganic Hybrid Materials" Mater. Sci. Eng. C 6, 167-174 (1998)

J. CesaranoIII, R. Segalman, P. Calvert "Robocasting" Ceramic Industry April 1998 94-102.

H.B.Denham, J. Cesarano III, B.H.King, P. Calvert "Mechanical behavior of Robocast alumina" in Solid Freeform Fabrication Proceedings 1998 eds. H.L. Marcus, J.J. Beaman, D.L. Bourell, J.W. Barlow and R.H. Crawford, U. Texas, Austin pp.589-593

P. Calvert, J. Peng, C. Souvignier, "Solid freeform fabrication of composites by direct deposition and by in situ mineralization" Mater. Res. Soc. Symp. Proc. 542 "Solid freeform and additive fabrication" eds. D. Dimos, S.C. Danforth, M.J.Cima, 1999, pp.3-12

U.S. Patent 5,906,863 (25 May 1999)

U.S. Patent 5,932,290 (3 August 1999).

T.B. Sercombe, GB Schaffer, P Calvert "Freeform fabrication of functional aluminium prototypes using powder metallurgy" J. Materials Sci. 34 (1999) 4245-4251

PERSONNEL SUPPORTED:
Graduate Students: Hugh Denham (PhD thesis in preparation), Sajiv Boggavarapu, Chad Souvignier (PhD thesis in preparation)
Undergraduate Students: Jeff Kersten, Lashel Devich

INTERACTIONS
This work has been discussed at many meetings. We are collaborating with Advanced Ceramics Research on the use of this freeforming technology in STTR projects to form a silicon nitride blisk, on bone implant materials and on nanotube composites. We are also helping them to commercialize this technique. We are working closely with Sandia National Labs. to apply this method to form ceramic-metal composite parts with a view to eventually replacing a critical component now used by Sandia.

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

0105

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 1/25/00	3. REPORT TYPE AND DATES COVERED FINAL REPORT 6/95-6/99

4. TITLE AND SUBTITLE
Smart Materials by Extrusion Solid Freeform Fabrication

5. FUNDING NUMBERS
AASERT F49620-95-1-0393 DEF

6. AUTHOR(S)
Paul Calvert

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Materials Science and Engineering,
University of Arizona Tucson AZ 85721

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/PKA
110 Duncan Ave, B115, Bolling AFB
Washington DC 20332

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Extrusion freeform fabrication has been used to build strong composite materials, materials with embedded sensors to monitor stress and degree of cure , and graded metal and ceramic composites. For fiber-reinforced composites it has been shown that orientation can be controlled by the writing process, allowing stiffness and strength to be varied from point to point within a component. A swelling and mineralization approach allows biomimetic composites to be made with high volume fractions of inorganic reinforcement and strengths up to 100 MPa. Studies of the response of parts with embedded stress sensors shows that the sensor response must be interpreted in light of stress sharing between the sensor and the host material. Freeforming offers a versatile route to many new material combinations. Potential applications include tough ceramics, desktop manufacturing and biomedical implants.

14. SUBJECT TERMS
Smart composites, Freeforming, Powder Metallurgy, Fiber orientation, Short-fiber composites

15. NUMBER OF PAGES
5

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT **UNCLASSIFIED**	18. SECURITY CLASSIFICATION ON THIS PAGE **UNCLASSIFIED**	19. SECURITY CLASSIFICATION OF ABSTRACT **UNCLASSIFIED**	20. LIMITATION OF ABSTRACT **UL**

NSN 7540-01-280-5500 **Standard Form 298 (Rev.2-89)**
Prescribed by ANSI Std. 239-18
298-102